Synthesis and Characterization of Dinuclear-Oxomolybdenum Complexes Containing Terephthalodihydrazide Ligands

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Under the guidance of

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CERTIFICATE

This is to certify that the dissertation entitled **"*Synthesis and Characterization of Dinuclear-Oxomolybdenum Complexes Containing Terephthalodihydrazide Ligands*"** submitted by Ashish Kumar Behera of Department of Chemistry, National Institute of Technology, Rourkela for the degree of Master of Science in Chemistry is based on the result obtain in the bonafide project work carried out by him under my guidance and supervision. To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/Institute for the award of any degree or diploma.

Date: 2-05-2011

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Date: 02.05.2011 Name: Ashish Kumar Behera

ABSTRACT

The reaction of new binuclear hexadentate diacylhydrazone ligands {where L = bis-(2-hydroxybenzaldehyde hydrazone of terephthalodihydrazine (TPHDS), bis-(2-hydroxyacetophenonehydrazone of terephthalohydrazine (TPHDO) and bis-(2-hydroxynapthaldehydehydrazone of terephthalohydrazine (TPHDN)} with the metal precursor ($MoO_2(acac)_2$) proceeds smoothly in refluxing ethanol to afford a three new dinuclear-dioxomolybdenum(VI) complexes $[Mo^{VI}O_2L(EtOH)]_2$. All the synthesized binuclear ligands and their corresponding metal complexes were successfully characterized by IR, UV- Vis, NMR spectroscopy and C, H, N analysis. The analytical data reveals that the metal complexes are a dinuclear octahedral one. The crystals were isolated from DMSO.

Introduction

Molybdenum is the metal which is placed in group 6 has atomic number 42 and atomic mass 95.94. It has chemical properties similar to those of chromium and tungsten. It has variable oxidation states which are from II to VI. It can coordinate ligands up to 8. Hence it can coordinate with a large number of ligands which may be organic or inorganic, or bridging ligands and it has a tendency to form binuclear as well as poly-nuclear complexes. Its complexes has many applications and thereby making its chemistry challenging. Molybdenum catalysts have wide range of applications in many of the fields. For example in fuel refining, conversion of coal to hydrocarbon liquids, synthesize raw materials for plastics and fibres, used in making alloys because it provides strength greater than that of steel. It is an important component of the enzyme nitrogenase that reduces atmospheric nitrogen to ammonia. Thus by exploiting its chemistry a large number of desired complexes can be synthesized. Cis dioxo complexes of molybdenum are exploited for the achiral and chiral epoxidation which is mentioned by Jin Zhao [1].

Molybdenum-based technical chemicals exploit the versatility of molybdenum chemistry in oxidation states. (VI), (V) and (IV). Materials made from molybdates are oxidation catalysts, are photoactive, and semiconducting. Many of the properties of molybdenum provide development opportunities and new commercial applications through the exploitation of its chemistry[2-6].

There are various applications of the aroyl hydrazones which depends upon their characteristics. Derivatives of aroyl hydrazone are effective to act as inhibitor to prevent the corrosion of the copper metal in presence of nitric acid. It is due to the electron donating capacity of those hydrazone ligands [7]. The ruthenium complex of aroyl hydrazone plays an important role in controlling the microbial growth. Aryl-aryl coupling can be carried out by ruthenium complexes of aroyl hydrazone. They also help in oxidation of alcohols [8]. Schiff bases have application in optical sensors as they show fluorescence properties over a particular pH range [9]. Transition metal complexes (Co(II), Cu(II), Ni(II), Fe(II), Mn(II)) with Schiff's bases have wide range of catalytic activities [10]. The hydrazones complexes have several applications in biological, pharmaceutical fields also.

In this dissertation I have reported the synthesis and characterization of three different aromatic carbonyls of terephthalodihydrazone (TPHD) ligands and their corresponding dioxomolybdenum(VI) complexes. All the synthesized ligands and corresponding metal complexes have been characterized by several spectroscopic techniques. The X-ray studies of few synthesized Mo complexes are under process.

Experimental Section

Synthesis of Hydrazide:

The 10 mmol of dimethyl terepthalate was taken in a round bottom flask. To it 20 mmol of hydrazine hydrate was added. 10 mL of ethanol was added for complete dissolution of reaction mixture.,Then reaction mixture was set for reflux five hours, then filtered and washed three times with ethanol and once with diethyl ether and dried over vacuo and over fused in $CaCl_2$.

Yield = 67% ; M. F: $C_8H_{10}N_4O_2$; C,H,N analysis: C: 6.15 (6.05); H: 7.60 (7.32); N 42.42(42.21).

Synthesis of Schiff's base ligands:

The Schiff's base ligand has been synthesized by taking the corresponding carbonyl compound and the prepared hydrazide in 1:2 ratio in reflux condition at room temperature using glacial acetic acid as solvent. The different schiff's base are given below

1.TPHDS

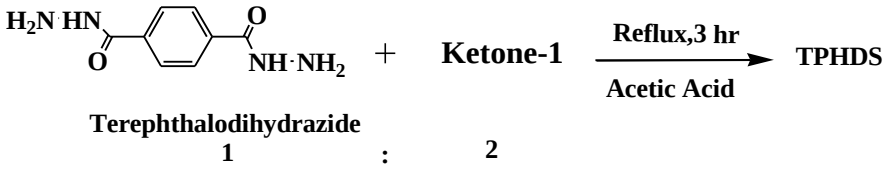


Figure-1

Yield =66% ;M. F: $C_{22}H_{18}N_4O_4$; C,H,N analysis: C:5.45 (5.47); H: 4.38 (4.47); N 0.95(0.99).

2.TPHDO:

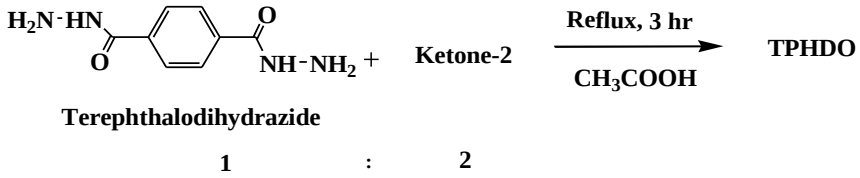


Figure-3

Yield = 53 % ; M. F: $C_{24}H_{22}N_4O_4$; C,H,N analysis: C:5.58 (5.67); H: 5.11 (5.15); N 0.90 (0.93).

3.TPHDN:

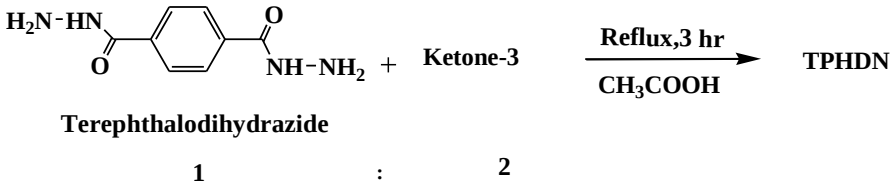


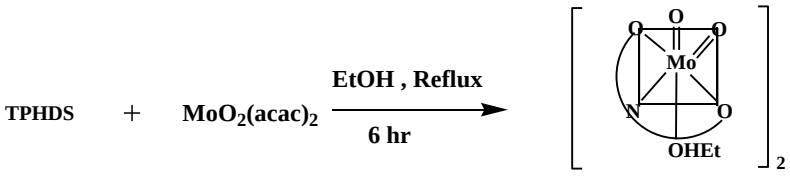
Figure-4

Yield =60 %; M. F: $C_{30}H_{22}N_4O_4$; C,H,N analysis: C:5.91 (5.97); H: 4.30 (4.38); N 0.75(0.79).

Synthesis of the Oxomolybdenum(VI) Complexes:

Complex 1: **$[Mo^{VI}O_2L^1(EtOH)]_2$**

The complex-1 has been synthesized by following methods.



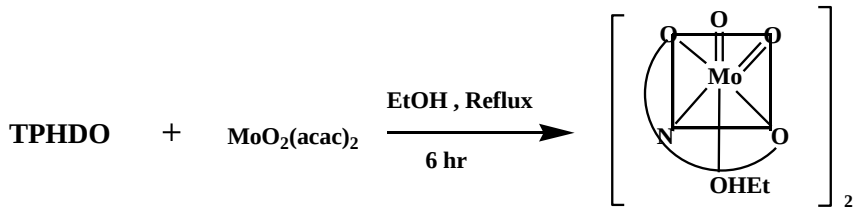
Dimeric Complex of dioxomolybdenum(VI)

Figure-5

Yield = 50%; M. F: $C_{26}H_{26}N_4O_{10}$; C,H,N analysis: C:4.00 (4.33); H: 4.00 (4.10); N 0.60 (0.32).

Complex 2:**$[Mo^{VI}O_2L^2(EtOH)]_2$**

The complex-1 has been synthesized by following methods.



Dimeric Complex of Dioxomolybdenum(VI)

Figure-6

Yield = 45%; M.F: $C_{28}H_{30}N_4O_{10}$; CHN values: C:4.12 (4.10); H: 4.42 (4.40); N 0.58(0.53).

Results and Discussions

Spectral characteristics:

IR Spectra of the ligand TPHDS and Complex 1$[Mo^{VI}O_2L^1(EtOH)]_2$:

Infrared spectra of all the ligands and complexes are taken in a KBR pellets. The complexes do not exhibit the ligand bands at ~3427 cm^{-1} [ν(OH)], ~3217 cm^{-1} [ν(NH)], and ~1661 cm^{-1} [ν(C=O)] [24,25] . Characteristic strong bands at ~1607 and ~1546 cm^{-1} due to ν(C=N) and ν(C=C/aromatic) stretching modes of the ligand [25] are located in the spectra of both the ligand and the complexes. The Mo=O stretching modes occur as a pair of sharp strong peaks in the 940-915 cm^{-1} range.

NMR of the ligand TPHDS:

The ^1H NMR spectrum of the free ligand exhibits an OH (phenolic) resonance at δ = 12.26 ppm, NH (imine) resonance at δ = 11.21 ppm and CH resonance at δ = 8.68 ppm. All the aromatic proton signals expected from it are clearly observed in the expected region at δ = 8.08 ppm-6.91 ppm. The conclusion was also supported by the results of ^{13}C NMR spectra which gives 22 distinct peaks as expected of the free ligand.

Electronic Spectra of complex 1 $[Mo^{VI}O_2L^1(EtOH)]_2$:

The electronic spectrum of this complexes were obtained at 411 nm by which it can be predicted that metal has bound to the ligand. The strong band at this position due to ligand to metal [L–Mo(dπ) LMCT] charge transfer [29]. Two strong absorptions are also located in the 265– 311 nm range, which are assignable to intraligand transitions. The UV-Vis spectrum of the complex was taken in DMSO.

IR Spectra of the ligand TPHDO and Complex 2$[Mo^{VI}O_2L^2(EtOH)]_2$:

The complexes do not exhibit the ligand bands at 3244 cm^{-1} [ν(OH)], 3065 cm^{-1} [ν(NH)], and 1673 cm^{-1} [ν(C=O)] [24,25] . Characteristic strong bands at ~1604 and ~1530 cm^{-1} due to ν(C=N) and ν(C=C/aromatic) stretching modes of the ligand [25]are located in the spectra of both the ligand and the complexes. The Mo=O stretching modes occur as a pair of sharp strong peaks in the 941-849 cm^{-1} range .

NMR of the ligand TPHDO:

The ^1H NMR spectrum of the free ligand exhibits an OH (phenolic) resonance at δ = 13.30 ppm,NH (imine) resonance at δ = 11.55 ppm and CH_3 resonance at δ = 3.90 ppm. All the aromatic proton signals expected from it are clearly observed in the expected regionat δ = 6.91 ppm-8.11 ppm.

Electronic Spectra of complex 2 $[Mo^{VI}O_2L^2(EtOH)]_2$:

The electronic spectrum of this complexes were obtained at 433 nm by which it can be predicted that metal has bound to the ligand. The strong band at this position due to ligand to metal [L–Mo(dπ) LMCT] charge transfer . Two strong absorptions are also located in the 274– 353nm range, which are assignable to intraligand transitions. The UV-Vis spectrum of the complex was taken in DMSO.

IR Spectra of TPHDN and Complex 3 $[Mo^{VI}O_2L^3(EtOH)]_2$:

Infrared spectra of all the complexes are mostly similar. The complexes do not exhibit the ligand bands at 3296 cm^{-1} [ν(OH)], 3015 cm^{-1} [ν(NH)], and 1678 cm^{-1} [ν(C=O)] . Characteristic strong bands at ~1605 and ~1534 cm^{-1} due to ν(C=N) and ν(C=C/aromatic) stretching modes of the

ligand [25]are located in the spectra of both the ligand and the complexes. The Mo=O stretching modes occur as a pair of sharp strong peaks in the 941-919 cm^{-1} range.

NMR of the ligand TPHDN & Complex 3 $[Mo^{VI}O_2L^3(EtOH)]_2$:

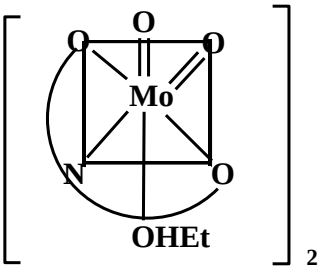
The ^1H NMR spectrum of the free ligand exhibits an OH (phenolic) resonance at δ = 12.68 ppm,NH (imine) resonance at δ = 12.40 ppm and CH resonance at δ = 9.51 ppm. All the aromatic proton signals expected from it are clearly observed in the expected regionat δ = 7.2 ppm-8.2 ppm. The signal for the OH proton disappears, indicating deprotonation of the phenolic OH group in the complexes.

Electronic Spectra of complex 3 $[Mo^{VI}O_2L^3(EtOH)]_2$:

The electronic spectrum of this complex was obtained at 466 nm by which it can be predicted that metal has bound to the ligand. The strong band at this position due to ligand to metal [L–Mo(dπ) LMCT] charge transfer. Two strong absorptions are also located in the 258– 346 nm range, which are assignable to intraligand transitions. The UV-Vis spectrum of the complex was taken in DMSO.

Proposed Structures:

As all the ligands have extensive π-delocalization across their backbone, so they try to remain in planar disposition. Thus they will occupy meridional planes in a distorted octahedral coordination sphere.



Dimeric Complex of Dioxomolybdenum(VI)

CONCLUSION

The hydrazides were prepared successfully with good yield. The corresponding binuclear schiff base TPHNS, TPHDO and TPHDN weresuccessfully prepared by condensation of terephthalodihydrazide with an aromatic carbonyl group. These binuclear ligands were used for the metallation with the metal precursor ($MoO_2(acac)_2$) to form their corresponding binuclear oxomolybdenum(VI) complexes. The complexes formed were successfully characterized by IR, UV,NMR spectroscopy and C, H, N analysis. The preliminary characterization data of these complexes have failed to indicate any definite coordination mode of ligands in them. To find out the binding mode(s) of ligands in these complexes, as well as their stereochemistry, x-ray structures of the corresponding complexesare required. The x-ray quality crystals of synthesised complexes have been sent for structure determination using X-ray crystallography.

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